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## VAPOR BARRIER COATING FOR POLYMERIC ARTICLES

Cross-Reference to Other Applications

5        This is a continuation-in-part of pending U. S. Patent Application No. 08/662,395, filed June 12, 1996.

Field of the Invention

10       The present invention relates generally to silicate-based barrier coatings for polymeric articles.

Background of the Invention

15       The coating of thermoplastic polymer substrates with moisture resistant barrier coating compositions to provide impermeability to gases such as oxygen, and liquids, is known [See, e.g., U.S. Patent 3,282,729]. Alkali metal polysilicates have long been known as protective coatings that modify the permeability or surface characteristics of polymeric films and other articles [See, e.g., US Patent No. 1,007,482; US Patent No. 1,424,425; US Patent No. 1,949,914; US Patent No. 3,102,038; US Patent No. 3,130,061; US Patent No. 3,180,747; US Patent No. 3,492,137; US Patent 3,522,066; US Patent No. 3,533,816 and US Patent No. 3,706,603].

25       Lithium (Li), potassium (K), and sodium (Na) polysilicate are used in coatings for a variety of surfaces. For example, Hecht and Iler, Canadian Patent No. 993,738, describe a gas and liquid-impermeable coating for polymeric substrates comprising lithium polysilicate having a mole ratio of  $\text{SiO}_2$  to  $\text{Li}_2\text{O}$  of  
30       between about 1.6 and 4.6.

Although alkali metal polysilicate barrier coatings do provide excellent vapor, gas and aroma barrier

properties to coated articles, the authors have found that some metal polysilicate barrier coatings display reduced oxygen barrier performance at relative humidities greater than about 60 percent. Additionally, polymeric  
5 films coated with said alkali metal polysilicate barrier coatings exhibit reduced barrier performance when subjected to repeated flexing.

Additionally, polymeric articles are known to become hazy after certain polysilicate coatings have been  
10 incorporated. The tendency of sodium polysilicate coatings to effloresce, i.e., to become covered by powdery crystalline material as a result of atmospheric exposure, has been documented [Weldes and Lange, Ind. Eng. Chem., 61(4):28-44 (1969)]. This characteristic has  
15 similarly been observed for lithium polysilicate coatings by the present inventors. In contrast, pure potassium polysilicate coatings do not effloresce, but suffer severe loss of barrier performance above 50 percent relative humidity. Pure lithium polysilicate coatings,  
20 on the other hand, exhibit little to no loss of barrier performance over the same relative humidity range.

Vermiculite, a layered silicate, has also been employed as an ingredient in coatings of various types. For example, US Patent 5,183,704 refers to so-called 2:1  
25 layered silicates, where the silicates are selected from mica and vermiculite. W. J. Ward et al, J. Membrane Science, 55:173-180 (1991) suggests vermiculite may provide the basis for a variety of improved coatings for films. It is stated that vermiculite could be used in a  
30 sprayed-on high barrier coating for low barrier plastics.

US Patent No. 5,244,729 refers to a polymeric film having a coating layer which comprises vermiculite platelets. See, also, US Patent No. 4,101,050 and

European patent applications No. 92305329.2, published December 16, 1992 as EP No. 518,647 and 92305330.0, published December 16, 1992 as EP No. 518,646.

Although layered silicates, including vermiculite, are known to form stable aqueous suspensions, these suspensions are also known to become destabilized in the presence of dissolved metal cations, such as those present in alkali metal polysilicates. Such destabilization results in flocculation of the layered silicates and reduces their efficacy in vapor, gas and aroma barrier applications.

There remains a need in the art for barrier coatings which overcome these deficiencies in prior art coatings.

#### 15 Summary of the Invention

In one aspect, the present invention provides a vapor barrier coating solution for polymeric articles comprising a layered inorganic mineral filler dispersed in an inorganic binder. In a desirable embodiment, the filler is a layered silicate and the binder is an alkali metal polysilicate. The weight fraction of the layered silicate in the dried coating ranges from above 0 to about 99 percent.

In a preferred aspect, a vapor barrier coating solution for polymeric articles comprises vermiculite dispersed in a solution of aqueous lithium polysilicate, wherein the weight fraction of the layered silicate in the dried coating ranges from above 0 to about 99 percent.

30 In still another aspect, the invention provides a polymeric article, such as a film or bottle, coated with the coating solutions described above. The polymer may

be a polyolefin, a polyester, or a polyamide, and may be biaxially oriented.

In yet another aspect, the invention provides a method of coating a polymeric article comprising the steps of (a) dispersing a layered inorganic mineral filler, e.g., a layered silicate in an inorganic binder, such as an aqueous alkali metal polysilicate suspension in an amount sufficient to create a suspension wherein the weight fraction of layered inorganic filler in the inorganic components of the dried coating from above 0 to about 99 percent, (c) coating the article using standard coating technology, d) drying the coated article, and (e) optionally laminating the barrier coated article. The coating, when dried, provides a high vapor barrier to the article.

In yet another aspect, the invention provides a method of increasing resistance of a barrier coating to loss of barrier properties due to flexing by incorporating into the barrier coating solution a layered, inorganic mineral filler with a high aspect ratio.

Other aspects and advantages of the present invention are described in the detailed description below and in the claims.

#### Detailed Description of the Invention

The present invention overcomes the deficiencies in prior art barrier coatings by providing a coating solution containing a layered inorganic mineral filler and an inorganic binder which provide high vapor barrier capability and flex resistance. Preferably, the coating solution comprises a metal polysilicate and layered silicate, which, when dried, provides excellent barrier

characteristics, especially at high relative humidity in comparison with coatings containing only metal polysilicates. The vapor barrier coating solution of the present invention may be applied to any polymeric article.

#### A. Definitions

The term "vapor" implies a liquid at partial pressure, such as water vapor. The term "gas" includes oxygen, nitrogen, carbon dioxide and others. "Aroma" includes those materials which bear a fragrance, for example, menthol and others. For simplicity, as used herein, the term "vapor barrier" can be interpreted to mean a barrier to gases and aromas as well as traditionally defined vapors.

Similarly as used herein, the term "solution" is interpreted to include colloidal dispersions and suspensions. By "colloidal dispersion or suspension" is meant any dispersion or suspension of particles in liquid, the particles being of a size greater than molecular scale that do not settle out. Generally the particle size in a suspension or dispersion of this invention are from about 10 to about 50,000 Angstroms. "Coating solution" as used herein is meant a liquid containing dissolved or suspended solids that do not settle out and which is used to apply said solids to a substrate.

#### B. Layered Inorganic Mineral Fillers

Useful layered fillers for the present invention include silicate materials such as phyllosilicates. Illustrative of such materials are smectite clay minerals such as bentonite, montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite,

magadiite, and kenyaite, vermiculite, and the like. Other useful layered materials include illite minerals such as ledikite and admixtures of illites with the clay minerals named above.

5 Other useful layered inorganic materials are layered double hydroxides, such as  $Mg_6Al_3(OH)_{18}(CO_3)_{1.7} \cdot H_2O$  (see W. T. Reichle, J. Catal., 94:549 (1985), which have positively charged layers and exchangeable anions in the interlayer spaces. Other layered materials having little  
10 or no charge on the layers may be useful in this invention provided they can be intercalated with swelling agents which expand their interlayer spacing. Such materials include chlorides such as  $ReCl_3$  and  $FeOCl$ , chalcogenides such as  $TiS_2$ ,  $MoS_2$ , and  $MoS_3$ , cyanides such  
15 as  $Ni(CN)_2$ , and oxides such as  $H_2Si_2O_5$ ,  $V_6O_{13}$ ,  $HTiNbO_5$ ,  $Cr_{0.5}V_{0.5}S_2$ ,  $W_{0.2}V_{2.8}O_7$ ,  $Cr_3O_8$ ,  $MoO_3(OH)_2$ ,  $VOPO_4 \cdot 2H_2O$ ,  $CaPO_4CH_3 \cdot H_2O$ ,  $MnHASO_4 \cdot H_2O$ ,  $Ag_2Mo_{10}O_{33}$ , and the like. Preferred swellable layered materials are phyllosilicates of the 2:1 type having a negative charge on the layers ranging  
20 from about 0.25 to about 0.9 charges per formula unit and a commensurate number of exchangeable cations in the interlayer spaces. See, other layered materials described in International Patent Application No. PCT/US92/06733, published on March 4, 1993 as WO93/04118.

25 A typical coating solution according to this invention may be prepared from commercially available layered silicates, preferably vermiculite. An exemplary commercially available aqueous dispersion of exfoliated vermiculite with a solids level of 7.5 percent by weight  
30 bears the trademark MicroLite® 963 Plus+ (W. R. Grace and Co.). Individual particles of this layered silicate are typically about 24-50 Angstroms thick and 10-22 microns in diameter, and thus possess very large aspect ratios,



i.e., the quotient of the lateral dimension of a platelet filler particle divided by its thickness.

C. *Inorganic Binders - Metal Polysilicates*

Solid metal polysilicates have intrinsic permeability much lower than organic polymers, making them attractive binder materials for thin barrier coatings containing layered mineral particles. The metal polysilicate is generally selected from lithium polysilicate, sodium polysilicate, potassium polysilicate or copolysilicate blends of these materials. In the present coating solutions, where layered silicates are employed, flocculation of the silicate platelets must be avoided. This requirement places stringent restrictions on the formulation of a barrier coating solution containing layered silicates and metal polysilicates.

Layered silicates have isoelectric points (iep), i.e., the pH at which the zeta potential is zero, of about 2.5. Layered silicates form stable sols at the high pH, about pH 10, of metal polysilicate barrier coating solutions. This stability can be compromised by cations that accumulate in the Stern layer, reduce the zeta potential of the particles and thereby lower the coulombic repulsion barrier to flocculation. The effectiveness of cations in causing flocculation is expressed as the critical flocculation concentration. This is the concentration above which flocculation is rapid. Divalent and trivalent metals cause flocculation at very low concentrations; they must be avoided in the coating solutions of the present invention. For example, W. R. Grace product literature recommends that "all additives to MicroLite® dispersions be nonionic in nature." Additionally, the same product literature lists the critical flocculation concentration for sodium ions

in the presence of MicroLite® dispersed vermiculites as 20 mmole/l. While prior art inventions that employ layered silicates in water soluble polymers or latexes adhere to this recommendation, the present invention does not. A  
5 typical coating solution of the present invention contains added lithium far in excess of the critical flocculation concentration. For example, a 7.5 weight percent solids coating solution, that when dried yields a coating comprising 20 weight percent lithium polysilicate  
10 ( $\text{SiO}_2:\text{Li}_2\text{O} = 4.05$ ) and 80 weight percent Microlite® dispersed vermiculite (see Example 2 below), contains 110 mmole/liter added lithium ion. While lithium ion is expected to be less destabilizing than sodium ion, the concentration of lithium ion in the above coating  
15 suspension is greater than what would be expected by one skilled in the art to result in a stable suspension.

Other factors, such as resistance of the metal polysilicate to efflorescence on exposure to atmospheric  $\text{CO}_2$ , favor the use of potassium polysilicate in a metal  
20 polysilicate coating solution. Potassium ion, however, would be expected by one skilled in the art to have a critical flocculation concentration similar to that of sodium.

Thus, where the layered silicate is vermiculite,  
25 which is susceptible to flocculation by cations, the preferred alkali metal polysilicate is lithium polysilicate. However, the formulation of a metal polysilicate coating solution containing dispersed vermiculite must be a compromise to balance solution  
30 stability and the other dried coating properties described above. One of skill in the art may adjust the relative ratios of the metal polysilicate to the layered

silica to achieve this balance in properties of the coating solutions.

A typical coating solution according to this invention may be prepared from commercially available metal polysilicates, such as lithium polysilicate, sodium polysilicate and/or potassium polysilicate solutions. An exemplary commercially available product bearing the trademark Inobond® Li 2043 (van Baerle & Cie AG) is an aqueous colloidal suspension of lithium polysilicate which contains ~24.5 percent by weight silicon dioxide and ~3.0 percent by weight lithium oxide. Another useful metal polysilicate product bears the trademark K-4009 (van Baerle & Cie AG) and is an aqueous colloidal suspension containing ~26.8 percent by weight silicon dioxide and ~13 percent by weight potassium oxide.

#### *D. Optional Surfactants*

These coating compositions can also contain a suitable surfactant to reduce surface tension. Preferably, the surfactant is nonionic. The surfactant selected should possess a critical micelle concentration sufficiently low to ensure a dried coating whose gas, vapor and aroma barrier properties are not compromised. Most preferably, the surfactant is selected from the group consisting of acetylenic diols and alkyl ethoxylates. One exemplary commercially available acetylenic diol bears the trademark Genapol® 26-L-60N (Hoechst Celanese). Two exemplary commercially available alkyl ethoxylates bear the trademarks Genapol® UD050 (Hoechst Celanese) and Dynol® 604 (Air Products). The amount of surfactant added to the coating composition will depend on the particular surfactant selected, but should be the minimum amount of surfactant that is necessary to achieve the uncompromised dried coating.

For example, typical surfactant amounts can be less than 0.1 percent by weight of an acetylenic diol or an alkyl ethoxylate.

*E. Method of the Invention*

- 5       The layered silicate-metal polysilicate coatings of the invention can be used on a variety of polymeric articles, polymeric films, polymeric sheets, rigid and semi-rigid polymeric containers and other surfaces to improve (i.e., reduce) the gas permeability of the
- 10 products. These coatings are particularly advantageous where the polymers used to prepare these articles do not provide sufficient vapor, gas or aroma impermeability for the desired application. Such polymers include
- 15 polyesters, such as poly(ethylene terephthalate) (PET); polyolefins, particularly polypropylene, polyethylene and cycloolefins (COC); such as a copolymer of ethylene and norbornene [US Patent No. 5,087,677]; and polyamides, such as nylon. Typically, polypropylene and PET films are biaxially oriented, depending on the customer
- 20 requirements. Especially preferred articles for coating with compositions of the present invention include polymeric films, bottles, jars, blisterpacks, and sheets commonly used in the food industry, containers and lidstocks, made of the foregoing polymers.
- 25       A typical coating solution according to this invention may be prepared from the above-described commercially available products. For instance, MicroLite® 963 Plus+ vermiculite, and either Inobond® Li 2043 lithium polysilicate or K-4009® potassium silicate suspension, or
- 30 both polysilicates, are mixed with water to produce a colloidal suspension having a desired solids content. One can also prepare the coating solutions of the invention by using the "parent" products which are used

to produce the commercially available polysilicates, but such preparation is well-known and unnecessary in view of the commercial availability of the lithium and potassium polysilicate solutions.

5       A typical useful solids content in the coating solution ranges from about 2 percent to about 10 percent by weight of solids. The desired solids content of the solution depends on the coating method used, as well as the specific coating formulation, and may be adjusted to  
10 achieve a thickness of between about 100 to about 500 nm of the dry coating. Preferably, where the components of the coating solution are vermiculite and lithium polysilicate, the solids content is between about 2 and about 8 percent by weight. Such an adjustment is well  
15 within the skill of the art [see, e.g., Canadian Patent No. 993,738].

After a period of stirring, a surfactant may be optionally added to reduce surface tension of the coating mixture. The barrier coating mixture is then ready to be  
20 applied to a polymeric surface. Conventional coating techniques, such as roll coating, spray coating, brush coating and dip coating, may be used. These techniques include, but are not limited to, roll, rod, reverse roll, forward roll, air knife, knife over roll, blade, gravure  
25 and slot die coating methods. General descriptions of these types of coating methods may be found in texts, such as *Modern Coating and Drying Techniques*, (E. Cohen and E. Guttoff, eds; VCH Publishers) New York (1992) and *Web Processing and Converting Technology and Equipment*,  
30 (D. Satas, ed; Van Nostrand Reinhold) New York (1984). Three dimensional articles may preferably be coated by spray coating or dip coating methods, among others. The method of application is not a limitation on the present

invention, but may be selected from among these and other well-known methods by the person of skill in the art.

The polymeric articles to be coated by the compositions of the invention may be previously  
5 untreated. Optionally, the polymeric article, such as a film or bottle, may be first plasma treated to improve wetting and adhesion by the barrier coating as described in the following Example 1. Alternatively, the polymeric  
10 article may be corona-treated by the industry-wide corona discharge treatment method. In instances where corona-treatment of the polymer does not cause suitable wetting of the coating on the polymer, a suitable primer may be first applied to the polymeric article. For example, in the case of polypropylene, a primer solution of  
15 poly(vinyl alcohol) or poly(hydroxystyrene) may be used to improve wetting of the polymer. The polymeric article or surface may also be flame treated or chemically etched or oxidized prior to the application of a primer solution or, alternatively, prior to the application of the  
20 coating solution of this invention.

Alternatively, the article may bear on at least one surface or side, a heat seal layer. Examples of such heat seal layers are an ethylene-propylene copolymer or ethylene-propylene-butylene terpolymer.

25 Exemplary polyolefin substrates used in the examples below are the FND xx and SCM xx grade biaxially-oriented polypropylene (BOPP) films produced by Trespaphan GmbH. The number, xx, refers to the film thickness in micrometers; thus FND 30 is a 30  $\mu\text{m}$  (or 1.2  
30 mil) thick BOPP film. These films are designed to be metallized by thermal or electron-beam evaporation of aluminum. FND and SCM grade BOPP films are three-layer laminates with thin heat-sealable layers on both sides.

One side of the film is corona treated at the factory to a surface energy of 36-39 dynes/cm to improve adhesion of aluminum. Supplemental corona treatment, immediately before applying a primer solution, was found to be  
5 beneficial even for these films that were corona treated at the factory. Similar commercially available polypropylene films that will be suitable in the present invention include AQS, MT BASE, and MVT BASE films (AET Packaging Films). These all have a heat seal layer on  
10 one side only and, in the case of AQS, a high energy treated surface for waterborne coatings. These are all intended to be coated on the side opposite from the heat seal layer.

Alternatively, the polymeric substrate may have  
15 a protective topcoat or laminate layer, such as polyurethane or Teflon<sup>®</sup>-type materials [DuPont]. Such topcoats or laminates may be selected by one of skill in the art, depending on the substrate and its intended use.

The coating mixture of this invention may be applied  
20 over or under such additional layers.

After coating the article, the resultant product must be dried at a selected temperature at or above room temperature. The selection of the drying temperature depends on the desired time for drying.  
25 Accelerated drying times may be achieved at elevated temperatures which would not be necessary if a longer time period for drying was acceptable. However, one of skill in the art can readily adjust the oven temperature and exposure time as desired. The performance of the  
30 dried barrier coating is insensitive to the drying temperature throughout the temperature range between about 25 to about 200°C.

The coating solutions according to this invention yield a dried coating that is substantially transparent at a thickness of less than 500 nm, the clarity improving with increased metal polysilicate fraction. These solutions provide a high vapor barrier capability, when dried, and are characterized by enhanced flex resistance on the coated article.

The following examples illustrate the preferred coating solutions and methods of the invention. These examples are illustrative only and do not limit the scope of the invention.

EXAMPLE 1: PREPARATION AND COATING OF LITHIUM-POTASSIUM COPOLYSILICATE BARRIER COATINGS CONTAINING DISPERSED VERMICULITE ON BIAXIALLY ORIENTED POLYPROPYLENE FILM

*A. Solution Preparation*

A one weight percent dispersion of Dynol® 604 surfactant (Air Products) was prepared by dispersing 10.0 g Dynol® 604 surfactant in sufficient distilled water to make 1000.0 ml of solution. This suspension was stirred vigorously immediately before use.

Solution A, a lithium-potassium copolysilicate solution having values of x and y of 0.5 and 3.64, respectively, for the formula  $(\text{Li}_2\text{O})_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$ , and containing 20 percent by weight solids, was prepared by stirring together 19.43 g distilled water, 12.90 g K-4009 solution, and 17.7 g Inobond® Li 2043 solution for ~30 minutes.

A series of lithium-potassium copolysilicate solutions containing dispersed vermiculite were prepared according to the amounts listed in Table I. Aqueous dispersions of MicroLite® dispersed vermiculite were prepared by diluting with distilled water the, as



received MicroLite® 963 Plus+ suspension containing 7.5 percent solids. These suspensions were then added to the appropriate amount of copolysilicate solution A. The surfactant solution was then added to the stirring mixture of vermiculite and copolysilicate. Solutions were not filtered before coating. All solutions had an overall solids level calculated to be 7.9 percent by weight. Sample solution C gelled immediately upon addition of the metal silicate solution and was not used further (see Table I).

#### *B. Film Preparation and Coating*

Four inch circles were cut from biaxially oriented Trespaphan® FND 20 polypropylene film (BOPP) (0.8 mil thick) with a scalpel. Any dust on the film was blown off with a jet of clean, filtered air. The film circles were then corona treated to improve wetting by polysilicate coating solutions and adhesion of dried polysilicate coatings. Corona treatment was performed using a Tantec Lab System II corona treater using a ceramic electrode with a 2 mm gap. The power setting was 90 percent, and the electrode was scanned over the film surface by hand for 20 s (approximately 10 passes). Approximately 10 g of the copolysilicate-vermiculite coating solution was dispensed on the polypropylene film. A spreading spin cycle of 300 rpm for 1 s was followed immediately by a spin cycle of 2000 rpm for 10 seconds. The coated films were dried in an oven maintained at 50°C for ~120 s. Several coated film samples were prepared with each coating solution.

#### *C. Oxygen Barrier Measurement*

Oxygen transmission rate (OTR) measurements were made using a Mocon instrument at 30°C and zero percent relative humidity. Table I presents the OTR values for

films prepared as described in the Example. As a point of reference, an uncoated sample of FND 20 film tested under the same conditions exhibited an OTR of  $2862 \text{ cm}^3/[\text{m}^2 \text{ day atm}]$ .

TABLE I  
Lithium-Potassium Copolysilicate-Dispersed Vermiculite  
Barrier Coatings on 0.8 mil Thick BOPP Film

Solution	Mass of Lithium- potassium copolysilicate solution A (g)	Mass of MicroLite® 963 Plus+ Dispersion (g)	Mass of Distilled Water (g)	Mass of 1% Dynol® 604 Solution (g)	Percent vermiculite in dry coating	O <sub>2</sub> Transmission Rate (cm <sup>3</sup> /[m <sup>2</sup> day atm] at 30°C/0% RH)
B	22.50	6.67	33.33	0.62	10	456
C	12.50	33.33	16.70	0.62	50	Solution gelled
D	2.50	60.00	0.00	0.62	90	2903

EXAMPLE 1. PREPARATION AND COATING OF LITHIUM POLYSILICATE  
BARRIER COATINGS CONTAINING DISPERSED VERMICULITE ON  
BIAXIALLY ORIENTED POLYPROPYLENE FILM

*A. Primer Preparation*

5        Finely ground polymer grade poly(para-hydroxystyrene)  
(Hoechst Celanese), 1.00 g, was added to 99.0 g of a 0.1 N  
aqueous solution of lithium hydroxide solution and heated at  
50°C until the solids were dissolved. The resulting brown-  
orange solution was filtered through fluted filter paper  
10 before use. A change in color of the solution from orange-  
brown to green-brown on standing overnight did not affect  
the performance of the solution as a primer.

*B. Coating Solution Preparation*

A series of colloidal solutions of lithium polysilicate  
15 barrier coating solutions containing dispersed vermiculite  
dispersion were prepared using the reagents and quantities  
listed in Table II by first diluting the MicroLite® 963  
Plus+ dispersion with distilled water and then adding  
Inobond® Li 2043 lithium polysilicate solution with  
20 stirring. Each suspension was stirred for 30 minutes  
immediately before coating and was not filtered. Each  
suspension had a total solids level of 7.5 percent by  
weight.

*C. Film preparation and coating*

25        Four inch circles were cut from Trespaphan® FND 20 BOPP  
film (0.8 mil thick) with a scalpel. Any dust on the film  
was blown off with a jet of clean, filtered air. The film  
circles were then corona treated as described in Example 1.  
Approximately 10 g of the poly(para-hydroxystyrene) primer  
30 solution was dispensed on the polypropylene film. A

spreading spin cycle of 300 rpm for 1 s was followed immediately by a spin cycle of 2000 rpm for 10 s. The coated films were dried in an oven maintained at 50°C for ~ 120 seconds.

- 5        After the priming process, approximately 10g of a polysilicate-vermiculite dispersion was dispensed onto the primed side of the polypropylene film. A spreading spin cycle of 300 rpm for 1 s was followed immediately by a spin cycle of 2000 rpm for 10 s. The coated films were dried in  
10    an oven maintained at 50°C for ~30 seconds.

*D. Oxygen barrier measurements*

- Oxygen transmission rate measurements were made using a Mocon instrument at 30°C under dry conditions. Table II presents the OTR values for films prepared as  
15    described in the Example. As a point of reference, a sample typical sample of uncoated FND 20 film tested under the same conditions exhibited an OTR of 2862 cm<sup>3</sup>/[m<sup>2</sup> day atm].

Table II  
Lithium Polysilicate-Dispersed Vermiculite  
Barrier Coatings on 0.8 mil Thick BOPP Film

Sample	Percent vermiculite in dry coating	Mass of MicroLite® 963 Plus+ Dispersion	Mass of Inobond® Li 2043	Mass of Distilled Water	O <sub>2</sub> Transmission Rate (cm <sup>3</sup> /[m <sup>2</sup> day atm]); 30°C 0% RH)
		(g)	(g)	(g)	
A	0	0	13.64	36.36	1161
B	10	5.07	12.25	32.68	1563
C	20	10.00	10.91	29.09	1662
D	40	20.00	8.18	21.82	1204
E	60	30.00	5.45	14.55	181
F	80	40.00	2.73	7.27	3
G	90	44.93	1.38	3.69	2
H	100	50.00	0	0	36

EXAMPLE 3: OXYGEN TRANSMISSION RATE VS. RELATIVE  
HUMIDITY OF BOPP FILM COATED WITH A LITHIUM  
POLYSILICATE-DISPERSED VERMICULITE BARRIER COATING

5 A sample of 0.8 mil thick BOPP film was primed and coated according to the method of Example 2 with the dispersed vermiculite-lithium polysilicate solution described in Example 2G (see Table II).

10 Oxygen transmission rate measurements were made using a Mocon instrument at 23°C. A sample was tested consecutively at 0, 40, 60, 70, 80, 90 and again at 0 percent relative humidities. The film was not removed from the sample chamber between measurements. Table III presents the measured oxygen transmission rates for  
 15 a typical sample tested in this manner.

Table III

Oxygen Transmission Rates vs. Relative Humidity for 0.8  
 mil Thick BOPP Film Coated with Lithium Polysilicate  
 20 Coating Containing 90 Percent by Weight Dispersed  
 Vermiculite

Percent Relative Humidity	Oxygen Transmission Rate (cm <sup>3</sup> /[m <sup>2</sup> day atm] at 23 °C)
0 - INITIAL	1
40	1
60	1
70	1
80	2
90	4
0 - FINAL	1

COMPARATIVE EXAMPLE 4: OXYGEN TRANSMISSION RATE VS.  
RELATIVE HUMIDITY OF BOPP FILM COATED WITH A LITHIUM-  
POTASSIUM POLYSILICATE BARRIER COATING

A sample of 0.8 mil BOPP film was primed and  
5 coated according to the method of Example 2 with a  
lithium-potassium copolysilicate solution containing 10  
percent solids by weight of the copolysilicate  
( $\text{Li}_2\text{O}$ )<sub>x</sub>( $\text{K}_2\text{O}$ )<sub>1-x</sub>( $\text{SiO}_2$ )<sub>y</sub>, wherein x, the mole fraction of  
 $\text{Li}_2\text{O}$  in the combined metal oxides,  $\text{M}_2\text{O}$ , is 0.5 and the  
10 y, the molar ratio of  $\text{SiO}_2:\text{M}_2\text{O}$ , is 3.64.

Oxygen transmission rate measurements were made  
using a Mocon instrument at 23°C. One sample, labeled  
A in this Example was tested at 0 percent relative  
humidity. A second sample, labeled B, was tested  
15 consecutively at 40, 60, 70, 80, 90, 0 percent relative  
humidities. This film was not removed from the sample  
chamber between measurements. Table IV presents the  
measured oxygen transmission rates for a typical sample  
tested in this manner.



Table IV

Oxygen Transmission Rates vs. Relative Humidity  
for 0.8 mil Thick BOPP Film Coated with  
Lithium-Potassium Copolysilicate Coating

5

Sample	Percent Relative Humidity	Oxygen Transmission Rate (cm <sup>3</sup> /[m <sup>2</sup> day atm] at 23 °C)
A	0	287
B	40	402
B	60	311
B	70	136
B	80	153
B	90	1022
B	0	1147

EXAMPLE 5: VERMICULITE-CONTAINING PRIMERS FOR METAL  
POLYSILICATE BARRIER COATINGS.

10 Another embodiment of the methods of this  
invention employs laying down an extremely thin (10-50  
nm) primer layer of a diluted coating of the present  
invention, i.e., about 1.0-2.5 percent by weight of the  
coatings of Example 1 containing both dispersed  
15 vermiculite and metal polysilicate. Upon the top of  
this layer is deposited an additional coating of a  
thicker layer of metal polysilicate from a more  
concentrated suspension not containing dispersed  
vermiculite. Such a composite barrier layer offers the  
20 advantages of improved barrier performance without the  
side effect of a slightly yellow color.

#### A. Coating Solution Preparation

A 2.5 weight percent aqueous dispersion of lithium polysilicate and dispersed vermiculite was prepared by  
5 diluting 10 g of the dispersion labeled G in Table II  
with 20 g of distilled water. The resulting dispersion  
was one in which 10 percent of the dry coating weight  
was lithium polysilicate and 90 percent of the dry  
coating weight was vermiculite.

10 A 10 percent solids solution was prepared of the  
copoly silicate  $(\text{Li}_2\text{O})_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$ , wherein x, the mole  
fraction of  $\text{Li}_2\text{O}$  of combined metal oxides  $\text{M}_2\text{O}$ , was 0.5  
and y, the molar ratio of  $\text{SiO}_2:\text{M}_2\text{O}$ , was 3.64. With  
continuous stirring 53.1 g of Inobond® Li 2043  
15 dispersion was diluted with 108.1 g of distilled water,  
followed by addition 38.8 g of K-4009 dispersion. The  
dispersion was stirred overnight and then filtered  
through Celite 545® diatomaceous earth. To the  
solution was added 2.0 g of the Dynol® 604 surfactant  
20 solution described in Example 1.

#### B. Film preparation and coating

Four inch circles were cut from Trespaphan® FND 15  
BOPP film (0.6 mil thick) with a scalpel. Any dust on  
the film was blown off with a jet of clean, filtered  
25 air. Approximately 10 g of primer solution described  
in Example 2A was dispensed on the polypropylene film.

A spreading spin cycle of 300 rpm for 1 second was  
followed immediately by a spin cycle of 2000 rpm for 10  
s. The coated films were dried in an oven maintained  
30 at 50°C for ~ 30 s.

After the priming process, approximately 10g of the polysilicate-vermiculite dispersion was dispensed on the primed side of the polypropylene film.

A spreading spin cycle of 300 rpm for 1 s was followed immediately by a spin cycle of 2000 rpm for 10 s. The coated films were dried in an oven maintained at 50°C for ~30 s. This coating process was repeated using the copolysilicate solution described above.

*C. Oxygen barrier measurements*

Oxygen transmission rate measurements were made using a Mocon instrument. An OTR of 66 cm<sup>3</sup>/[m<sup>2</sup> day atm] was measured at 23°C and at 0 percent relative humidity for a film prepared in the manner above. For comparison, a sample of uncoated FND 15 film exhibits an OTR of 2250 cm<sup>3</sup>/[m<sup>2</sup> day atm] under the same conditions.

EXAMPLE 6: ROLL COATING OF LITHIUM POLYSILICATE-  
DISPERSED VERMICULITE COATINGS ONTO BIAXIALY ORIENTED  
POLYPROPYLENE FILM

*A. Primer Preparation*

A poly(vinyl alcohol) primer solution was prepared. Poly(vinyl alcohol) (Aldrich, 98-99% hydrolyzed, average M<sub>w</sub>, 85,000-146,000; 30.0 g) was added to 3000 g distilled water. The mixture was heated to 80°C and stirred until dissolution of polymer appeared complete. A water clear solution was obtained by filtering the hot solution through fluted filter paper. To the cooled solution was added 0.3 g Dynol® 604 nonionic surfactant.

A one weight percent solution of poly(para-hydroxystyrene) in 0.1 N aqueous lithium hydroxide, PHS, was prepared by adding 30.0 g of finely ground polymer grade poly(para-hydroxystyrene) (Hoechst Celanese) to 3000 g of 0.1 N aqueous lithium hydroxide and heated at 50°C until the solids are dissolved. The resulting brown-orange solution was filtered through fluted filter paper before use. After cooling, 0.3 g of Dynol® 604 nonionic surfactant was added to the solution with stirring. A change in color of the solution from orange-brown to green-brown on standing overnight did not affect the performance of the solution as a primer.

*B. Solution Preparation and Coating*

Solutions of lithium polysilicate-dispersed vermiculite were prepared using the amounts shown in Table V and using the procedure described in Example 3. Trespaphan® FND 20, biaxially oriented polypropylene film (0.8 mil thick) was run through a multiple stage reverse gravure roll coater such that a primer layer of poly(para-hydroxystyrene) or PVOH was applied and dried, followed by application and drying of a lithium polysilicate-dispersed vermiculite coating solution of this example.

*C. Oxygen Barrier measurement*

Oxygen transmission rate measurements were made using a Mocon instrument at 30°C under dry conditions. Table V presents OTR results for films described in the Example.

Table V  
Lithium Polysilicate Containing Dispersed Vermiculite Barrier Coatings Applied by Reverse Gravure Roll  
Coating to 0.8 mil Thick BOPP Film

Experiment	Primer Used	Percent by weight vermiculite in dried coating	Total Solution Percent solids	MicroLite® 963plus+ Dispersion	Mass Inobond® Li 2043 (g)	Mass Distilled Water (g)	O <sub>2</sub> Transmission Rate (cm <sup>3</sup> /[m <sup>2</sup> day atm]); 30°C 0% RH
A	PHS	80	7.5	2400	164	436	263
B	PVOH	80	2.5	800	54.5	2145	395
C	PVOH	60	2.5	600	109	2291	210
D	PVOH	60	5.0	1200	218	1582	168
E	PVOH	60	7.5	1800	327	872	122

EXAMPLE 7: ROLL COATING OF LITHIUM POLYSILICATE-  
DISPERSED VERMICULITE COATINGS ONTO POLY(ETHYLENE  
TEREPHTHALATE) FILM

A. *Solution Preparation and Coating*

5           Solutions of lithium polysilicate-dispersed  
vermiculite were prepared using the amounts shown in  
Table VI and using the procedure described in Example  
3. Hostaphan® 2400, biaxially oriented poly(ethylene  
terephthalate) (0.5 mil thick) film was run through a  
10 multiple stage reverse gravure roll coater such that a  
primer layer of poly(para-hydroxystyrene), PHS, or PVOH  
was applied and dried, and followed by application and  
drying of a lithium polysilicate/dispersed vermiculite  
coating solution. Both coating and drying were  
15 accomplished using a reverse gravure roll coating  
process.

B. *Oxygen Barrier Measurement*

Oxygen transmission rate measurements were  
made using a Mocon instrument at 30°C under dry  
20 conditions. Table VI presents the measured oxygen  
transmission rates for film samples prepared in this  
manner. As a point of reference, uncoated PET film  
used in this example exhibits a typical OTR of 170  
cm<sup>3</sup>/[m<sup>2</sup> day atm] when tested under the same conditions.

Table VI  
Lithium Polysilicate Containing Dispersed Vermiculite Barrier Coatings Applied by Reverse Gravure Roll  
Coating to 0.5 mil Thick PET Film

Experiment	Primer Used	Percent by weight vermiculite in dried coating	Total Solution Percent Solids	Mass of MicroLite® 963Plus+ Dispersion	Mass of Inobond® Li 2043	Mass of Distilled Water	O <sub>2</sub> Transmission Rate (cm <sup>3</sup> /m <sup>2</sup> day atm); 30°C 0% RH)
				(g)	(g)	(g)	
A	PHS	80	7.5	2400	164	436	18
B	PVOH	60	7.5	1800	327	872	1

EXAMPLE 8: FLEX TESTING PET FILM COATED WITH A LITHIUM  
POLYSILICATE BARRIER COATING CONTAINING DISPERSED  
VERMICULITE

5 A sample of the biaxially oriented PET film primed  
with PVOH and barrier coated with a lithium polysilicate-  
vermiculite blend as described in Example 7 was subjected  
to 50 flex cycles in a standard Gelbo flex testing  
machine. Oxygen transmission rate measurements were made  
using Mocon instrument at 30°C under dry conditions. The  
10 OTR of the flexed film was measured to be 670 cm<sup>3</sup>/[m<sup>2</sup> day  
atm] at 30°C and 0 percent relative humidity. This is  
approximately a five-fold increase in OTR from the  
measured OTR for an unflexed sample of this film.

15 COMPARATIVE EXAMPLE 9: FLEX TESTING PET FILM COATED WITH  
A LITHIUM-POTASSIUM COPOLYSILICATE BARRIER COATING

A. *Solution Preparation and Coating*

A lithium-potassium copolysilicate coating solution  
prepared as described in Example 4 was diluted with an  
20 equivalent mass of distilled water. The resulting  
solution contained 5 percent by weight solids of the  
copolysilicate (Li<sub>2</sub>O)<sub>x</sub>(K<sub>2</sub>O)<sub>1-x</sub>(SiO<sub>2</sub>)<sub>y</sub>, wherein x, the mole  
fraction of Li<sub>2</sub>O of combined metal oxides M<sub>2</sub>O, was 0.5 and  
y, the molar ratio of SiO<sub>2</sub>:M<sub>2</sub>O, was 3.64.

25 Hostaphan® 2400, biaxially oriented poly(ethylene  
terephthalate) (0.5 mil thick) film was run through a  
multiple stage reverse gravure roll coater such that a



primer layer of PVOH (Example 6A) was applied and dried, and followed by application and drying of the copolysilicate coating solution described in this example. Both coating steps were accomplished using a reverse gravure roll coating process.

*B. Flex Testing and OTR Measurements*

A sample of the biaxially oriented PET film primed with PVOH and barrier coated with the copolysilicate described above was subjected to 50 flex cycles in a standard Gelbo flex testing machine. Oxygen transmission rate measurements were made using instrument at 30°C under dry conditions. The OTR of the flexed film was measured to be 1231 cm<sup>3</sup>/[m<sup>2</sup> day atm] at 30°C and 0 percent relative humidity. This is approximately a nine-fold increase in OTR from the measured OTR for an unflexed sample of this film.

EXAMPLE 10: AIR KNIFE COATING OF LITHIUM POLYSILICATE-DISPERSED VERMICULITE COATINGS ONTO BIAXIALY ORIENTED POLYPROPYLENE FILM

Hostaphan<sup>®</sup> 2400, biaxially oriented poly(ethylene terephthalate) film (Hoechst Diafoil, 0.5 mil thick) was coated with an aqueous primer solution containing 1 percent poly(para-hydroxystyrene), 0.01 percent Dynol<sup>®</sup> 604 surfactant, and 0.02 percent Genapol<sup>®</sup> UD050 surfactant by weight in 0.1 N lithium hydroxide and subsequently dried. The resulting primed film was then coated with the solution labeled E in Table V by an air

knife process and subsequently dried. Oxygen  
transmission rate measurements performed on a Mocon  
instrument at 23 °C and 0 percent relative humidity  
resulted in an average OTR value of  $2.7 \pm 1.8 \text{ cm}^3/[\text{m}^2 \text{ day}$   
5 atm] for 8 samples.

All references and patents cited above are  
incorporated herein by reference. Numerous modifications  
and variations of the present invention are included in  
10 the above-identified specification and are expected to be  
obvious to one of skill in the art. Such modifications  
and alterations to the compositions and processes of the  
present invention are believed to be encompassed in the  
scope of the claims appended hereto.

## WHAT IS CLAIMED IS:

1. A vapor barrier coating solution for polymeric articles comprising:

- 5 (a) a metal polysilicate solution and  
(b) a layered silicate.

2. The solution according to claim 1 wherein said layered silicate is selected from the group consisting of bentonite, vermiculite, montmorillonite, nontronite, beidellite, volkonskoite, hectorite,  
10 saponite, sauconite, magadiite, kenyaite, ledikite and admixtures thereof.

3. The solution according to claim 1 wherein said metal polysilicate is a copolysilicate of lithium and potassium of the formula  $(\text{Li}_2\text{O})_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$ , wherein  
15  $x$  is between 0 and 1 and  $y$  is between 1 and 10.

4. The solution according to claim 1 wherein said metal polysilicate is a copolysilicate of lithium and potassium of the formula  $(\text{Li}_2\text{O})_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$ , wherein  
 $x$  is between 0.5 and 1 and  $y$  is between 1 and 10.

20 5. The solution according to claim 1 wherein said metal polysilicate is lithium polysilicate.

6. The coating solution according to claim 1 wherein said layered silicate is substantially exfoliated vermiculite.

7. The coating solution according to claim 1, which yields a dried coating that is substantially transparent at a thickness of less than 500 nm.

8. The coating solution according to claim 1  
5 wherein said layered silicate comprises up to 99 percent by weight of the inorganic solids in said solution.

9. The coating solution according to claim 1 wherein said layered silicate comprises between 40 and 90 percent by weight of the inorganic solids in said  
10 solution.

10. The coating solution according to claim 1, additionally comprising a suitable surfactant.

11. The coating solution according to claim 10, wherein the surfactant is nonionic and possesses a  
15 critical micelle concentration sufficiently low to ensure a dried coating uncompromised by residual surfactant.

12. The coating solution according to claim 11, wherein the surfactant is selected from the group consisting of acetylenic diols and alkyl ethoxylates.

20 13. A barrier coated polymeric article comprising:

(a) a polymeric substrate and

(b) an inorganic barrier layer, comprising a dried coating of the solution of claim 1.

14. The article according to claim 13 wherein said substrate is selected from the group consisting of a polymeric film, a polymeric sheet, and a rigid or semi-rigid polymeric container.

5           15. The article according to claim 14 wherein said substrate is a film that contains on at least one side a heat seal layer.

16. The article according to claim 13 wherein said polymer is a polyolefin, a polyester, or a  
10 polyamide.

17. The article according to claim 16 wherein said polyester is poly(ethylene terephthalate).

18. The article according to claim 13 wherein said polyolefin is polypropylene, polyethylene or a  
15 cycloolefinic copolymer.

19. The article according to claim 18 wherein said cycloolefinic copolymer is a copolymer of ethylene and norbornene.

20. The article according to claim 16 wherein  
20 said polyamide is nylon.

21. The article according to claim 16 wherein said polymer is biaxially oriented.

22. The article according to claim 13 wherein said article further comprises a protective topcoat or laminate layer.

23. The article according to claim 13 wherein  
5 the substrate is plasma treated, corona treated, flame treated, or chemically etched or oxidized.

24. A method of making a humidity resistant high gas, vapor and aroma barrier coating for polymeric film comprising coating said article with the coating  
10 solution of claim 1.

25. A method of making a high gas, vapor and aroma barrier coating for polymeric film comprising coating said article with the coating solution of claim 1.

15 26. A method for imparting flex resistance to alkali metal polysilicate barrier coating comprising adding to said coating solution a layered inorganic mineral filler which contributes to providing high vapor barrier capability when coated onto an article and dried.

20

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/09906

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09D1/02 C08J7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 084 266 A (FUJII MINORU) 27 July 1983 see page 7, line 14-16 see page 16, line 15-18; claims 1-3 ---	1,2,5,9
X	DATABASE WPI Section Ch, Week 8508 Derwent Publications Ltd., London, GB; Class L02, AN 85-047068 XP002043002 & JP 60 005 057 A (TOYOTA CENT RES & DEV LAB), 11 January 1985 see abstract --- -/--	1,2,9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

International Application No.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 7751 Derwent Publications Ltd., London, GB; Class G02, AN 77-91268Y XP002043003 & JP 52 135 339 A (NISSHIN ENG CO LTD) , 12 November 1977 see abstract	1,2,5
X	--- EP 0 108 827 A (SCHWIETE ROLF DR.) 23 May 1984 see claim 1; example 1	1,2
A	--- LU 67 779 A (DU PONT DE NEMOURS) 21 December 1973 * whole document * & CA 993 738 A cited in the application	1,13
A	--- EP 0 518 647 A (ICI) 16 December 1992 cited in the application see claims -----	1,13



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/09906

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 84266 A	27-07-83	JP 1598802 C JP 2018314 B JP 58120556 A AU 536014 B AU 9197682 A CA 1194253 A US 4802921 A	28-01-91 25-04-90 18-07-83 12-04-84 07-07-83 01-10-85 07-02-89
EP 108827 A	23-05-84	NONE	
LU 67779 A	21-12-73	BE 800699 A CA 993738 A DE 2329749 A FR 2187543 A GB 1424425 A NL 7308122 A	10-12-73 27-07-76 03-01-74 18-01-74 11-02-76 14-12-73
EP 518647 A	16-12-92	AT 147089 T AU 648673 B AU 1821392 A CA 2071058 A CN 1069988 A DE 69216303 D DE 69216303 T ES 2096722 T JP 5177782 A US 5571614 A	15-01-97 28-04-94 17-12-92 15-12-92 17-03-93 13-02-97 15-05-97 16-03-97 20-07-93 05-11-96

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